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Pd nanocrystals with continuously tunable high-index facets as a model nanocatalyst

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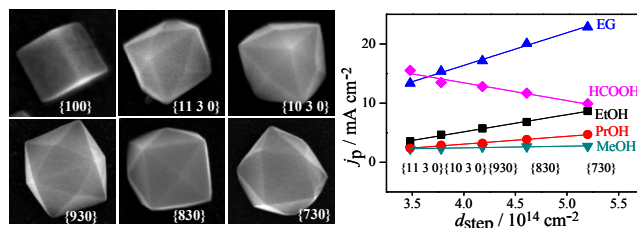
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ABSTRACT. Knowledge of the structure–reactivity relationship of catalysts is usually gained through using well-defined bulk single-crystal planes as model catalysts. However, there exists a huge gap between bulk single-crystal planes and practical nanocatalysts in terms of size, structural complexity, and local environment. Herein, we efficiently bridged this gap by developing a model nanocatalyst based on nanocrystals with continuously tunable surface structures. Pd nanocrystals with finely tunable facets, ranging from a flat {100} low-index facet

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3 to a series of $\{hk0\}$ high-index facets, were prepared by an electrochemical square-wave
4 potential method. The validity of the Pd model nanocatalyst has been demonstrated by structure–
5 potential method. The validity of the Pd model nanocatalyst has been demonstrated by structure–
6 reactivity studies of electrocatalytic oxidation of small organic molecules. We further observed
7 that Pd nanocrystals exhibited catalytic performance considerably different from bulk Pd single-
8 crystal planes with the same Miller indices. Such differences were attributed to special catalytic
9 functions conferred by nanocrystal edges. This study paves a promising route for investigating
10 catalytic reactions effectively at the atomic and nano- scales.
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23 **KEYWORDS.** High-index facets; model catalysts; single crystalline planes; electrocatalysis;
24 electrooxidation; structure–reactivity relationship
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30 Graphical Abstract



INTRODUCTION

Heterogeneous catalysis and electrocatalysis are widely applied in energy conversion and storage, oil refining and environmental decontamination.¹⁻² Catalytic reactions occur only on catalyst surfaces and are thus very sensitive to the surface structure.³⁻⁴ Understanding the structure–reactivity relationship at the atomic level is of fundamental importance for rational design of high-performance catalysts, and has long been a central concern in surface science and catalysis communities.⁴⁻¹¹ Practical catalysts consist of nanoparticles with abundant edge and corner sites, which typically serve as active sites.¹²⁻¹⁵ However, practical nanocatalysts cannot be directly used for structure–reactivity studies due to their structural complexity and non-uniformity.

A strategy to overcome this hurdle is to use two-dimensional (2D) single-crystal planes with well-defined atomic arrangement as model catalysts. This strategy was originally proposed by Langmuir in 1922,¹⁶ but only became experimentally accessible in the 1960s. As pioneers, Ertl⁵ and Somorjai¹⁷ developed model catalysts by using bulk single-crystal planes in heterogeneous catalysis, and Clavilier¹⁸ made an initial contribution to electrocatalysis. Alternative model catalysts that consist of nanoparticles supported on single-crystal planes have also been developed for investigating support effects.⁶ Although the bulk single-crystal model catalyst approach has provided valuable knowledge about surface sensitivity and active sites, etc. there exists a long-standing open question regarding a huge gap between bulk single-crystal planes and practical nanocatalysts in terms of size, structural complexity, and local environments, as illustrated in Figure 1. Bulk single-crystal planes have a macro size of millimeter scale, which is approximately six orders of magnitude larger than the nanometer size of practical catalysts, and have 2D long-range ordered surface structures. By contrast, practical nanocatalysts consist of 3D

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3 nanoparticles with complex and irregular surface structures. Such a huge gap can lead to intrinsic
4 differences in their catalytic behavior. For example, although bulk Au is inert for CO oxidation,
5 Au nanoparticles smaller than 5 nm exhibit an exceptionally high activity for this reaction.¹⁹
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10 To bridge this gap, new-generation model catalysts based on nanocrystals (NCs) must be
11 developed. These NCs should have particle sizes and edge sites comparable to those of practical
12 nanocatalysts while retain well-defined and tunable surface structures as bulk single-crystal
13 planes (Figure 1). Clearly, the prerequisite for this approach is structure-controlled synthesis of
14 NCs, particularly NCs with continuously tunable high-index facets (i.e., gradually tunable atomic
15 terrace-step structures) to reveal the catalytic properties of active step/edge sites of practical
16 nanocatalysts. To date, NCs of three low-index facets (i.e., {111}, {100}, and {110} facets)²⁰⁻²³
17 and limited cases of high-index facets have been reported.²⁴⁻²⁹ However, continuously tuning of
18 high-index facets remains a challenge, which mainly arises from two aspects: (i) High-index
19 facets have a high surface energy, which results in rapid disappearance of high-index facets
20 during the NC growth; (ii) The Miller indices of high-index facets are continuously variable, and
21 the difference in the surface energy of two adjacent high-index facets is very small (Figure S1 in
22 the Supporting Information), leading to a broad distribution of the surface structures on the
23 resultant NCs.
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44 Tetrahedral (THH) Pt and Pd NCs with {730} high-index facets were firstly synthesized
45 in our laboratory by developing an electrochemical square-wave potential (SWP) method.^{24,30}
46 The formation of high-index facets was mainly attributed to the SWP-driven repetitive
47 adsorption/desorption of oxygen species through H₂O dissociation, which induced the formation
48 of step sites on the surfaces through a site-exchanged mechanism.²⁴ A THH NC has 24 {hk0}
49 high-index facets, which can be regarded as a cube with each face capped by a square-based
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3 pyramid. The Miller indices (i.e., the values of h and k) and the density of step sites (d_{step}) can be
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5 altered theoretically by changing the geometric parameters of the THH NCs, such as the
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7 interfacial angles or the ratio of pyramid height to cube edge length (Figure S1 and Table S1 in
8
9 the Supporting Information).
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13 In this study, we synthesized a series of Pd NCs with continuously tunable surface structures
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15 ranging from $\{100\}$ low-index facets to a set of $\{hk0\}$ high-index facets by utilizing the
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17 electrochemical SWP method. The as-synthesized Pd NCs were served as a model nanocatalyst
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19 to study the structure–reactivity relationship at the atomic level and nanoscale, for
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21 electrocatalytic oxidation of small organic molecules relevant to direct fuel cells. Significantly
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23 different electrocatalytic behaviors towards ethanol oxidation were observed between Pd NCs
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25 and bulk Pd single-crystal planes with the same Miller indices, and correlated to the severe
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27 poisoning effect by edge sites on NCs. This study demonstrates an effective route to bridge the
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29 aforementioned gap in catalysis research between bulk single-crystal planes and practical
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31 nanocatalysts.
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36 37 RESULTS AND DISCUSSION 38

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40 **Characterization of Pd NCs with continuously tunable facets.** Figure 2A shows scanning
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42 electron microscope (SEM) and transmission electron microscope (TEM) images of the as-
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44 prepared Pd NCs with different surface structures. The overall morphology, size distribution, and
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46 surface structures are demonstrated in Figure S2-S7 in the Supporting Information. All samples
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48 had a similar average particle size of approximately 80 nm. The surface structures of the NCs
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50 were controlled by varying the upper potential (E_U) of the SWP. The higher E_U corresponds to
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52 the more intensive oxygen adsorption on the Pd surface, which facilitates the formation of more
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3 stepped facets. As the E_U increased from 0.950 V to 1.040 V, the shapes of the Pd NCs changed
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5 from a cube of $\{100\}$ facets (denoted as Cube $\{100\}$) to a series of THH of $\{hk0\}$ high-index
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7 facets (denoted as THH $\{hk0\}$). To determine the Miller indices of THH Pd NCs, TEM images of
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9 Pd NCs along the $[001]$ orientation were captured. In this orientation, eight side facets parallel to
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11 the $[001]$ axis can be imaged edge-on and form an octagonal projection, as illustrated in Figure
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13 S1 and Figure 2A. The Miller indices were calculated according to the interfacial angle α ($\alpha =$
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15 $2\arctan(h/k)$).^{24, 31} For the THH NCs prepared by the SWP method with the E_U of 1.000, 1.010,
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17 1.020, 1.030 and 1.040 V, the Miller indices varied continuously from $\{11\ 3\ 0\}$, $\{10\ 3\ 0\}$, $\{930\}$,
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19 $\{830\}$ to $\{730\}$. The surface structure of these Pd NCs was uniform. For example, TEM images
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21 of more than 20 THH $\{830\}$ Pd NCs along the $[001]$ direction were captured (Figure S8). The
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23 distribution of the interfacial angle α (four α on each NC) was very narrow with a standard
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25 deviation of around 1° (Figure 2B). This variance was essentially equal to the angle deviation of
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27 bulk single-crystal planes. Therefore, the surface structure of the as-prepared Pd NCs was
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29 adequately uniform for structure–reactivity studies. Furthermore, the high-index facets of Pd
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31 NCs were very stable in the electrochemical tests as benefited from their harsh growth conditions
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33 consisting of repeated oxidation-reduction cycling induced by the SWP. For example, both the
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35 voltammetric characteristic and the shape/Miller index of THH $\{830\}$ Pd NCs changed little after
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37 subjected to 5000 potential cycles between 0.1 and 1.1 V in 0.1 M HClO₄ (Figure S9).
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46 Figure 2A also illustrates the atomic arrangements of the facets of the as-prepared Pd NCs.
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48 They consisted of $\{100\}$ terrace followed by $\{110\}$ step periodically. Alternatively, the $\{730\}$
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50 facet can be considered as two $\{210\}$ subfacets followed by one $\{310\}$ subfacet periodically, and
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52 $\{830\}$ facet as two $\{310\}$ subfacets followed by one $\{210\}$ subfacets, and $\{10\ 3\ 0\}$ facet as two
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54 $\{310\}$ subfacets followed by one $\{410\}$ subfacets etc. The d_{step} increased in the order of $\{100\}$
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3 << {11 3 0} < {10 3 0} < {930} < {830} < {730} (Figure S1 and Table S1), as confirmed by the
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5 electrochemical voltammetric characterization in 0.1 M HClO₄ electrolyte solution (Figure 2C),
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7 where the current peaks at around 0.15 and 0.20 V were attributed to the hydrogen
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9 adsorption/desorption on Pd {110} steps and {100} terraces, respectively.³² As expected, the
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11 former was strengthened as the Miller indices varied from {100} to {730}. Step sites are
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13 favorable for oxygen adsorption at a low potential. As a result, the integral charge of oxygen
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15 adsorption on Pd step sites from 0.70 to 0.90 V increased linearly with the calculated d_{step} on the
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17 THH NCs (Figure 2D). The surface structure of Pd NCs was further characterized by CO
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19 stripping (Figure S10). The peak potentials of CO oxidation shifted positively with increasing the
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21 d_{step} . The low-coordinated step sites facilitate the adsorption of both CO and the surface O/OH
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23 formed from water dissociative adsorption. The former is unfavorable for CO oxidation, while
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25 the latter is favorable for the oxidation reaction. The positively shifting of CO stripping peak
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27 potential with increasing step sites may indicate that the strength of the CO adsorption dominates
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29 the oxidation reaction, the latter is very sensitive to the surface structure and is consistent with
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31 the continuous change of the surface structure from {100} to {730} facets.
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39 **Structure–reactivity relationship revealed by the model nanocatalyst.** The continuously
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41 tunable high-index facets of Pd NCs can be served as a model catalyst for structure–reactivity
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43 studies at nanoscale. Figure 3A illustrates voltammograms of electrocatalytic oxidation of a
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45 series of fuel cell-related small organic molecules, including formic acid, methanol, ethanol, n-
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47 propanol, and ethylene glycol. The surface-structure sensitivity is greatly different for these
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49 electrocatalytic reactions. As the d_{step} increased, the catalytic activity markedly increased for
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51 multi-carbon alcohol (ethanol, n-propanol, and ethylene glycol) oxidation, and changed little for
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53 methanol oxidation, but decreased for formic acid oxidation (Figure 3B). In addition, high-index
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3 facets (such as THH{730}) exhibited relatively lower peak potentials for the electrooxidation of
4 these small organic molecules in comparison to the low-index facets, which could be related to
5 the facile formation of inert surface oxides on the highly stepped surface.³³
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11 To quantitatively evaluate the surface-structure sensitivity, both the peak current density (j_p)
12 and d_{step} were normalized to the values obtained on the least stepped THH{11 3 0} Pd NCs. As
13 shown in Figure 3C, the normalized activity ($j_{p\{hk0\}}/j_{p\{11\ 3\ 0\}}$) was linearly related to the
14 normalized step density ($d_{\text{step}\{hk0\}}/d_{\text{step}\{11\ 3\ 0\}}$), yielding slopes of 2.93, 1.99, 1.35, 0.10, and -0.62
15 for the oxidation of ethanol, n-propanol, ethylene glycol, methanol, and formic acid, respectively.
16 These slopes represented the influence of surface structure on catalytic activity. Multi-carbon
17 alcohol oxidation exhibited a significant surface-structure sensitivity and could be ranked in
18 order of ethanol > n-propanol > ethylene glycol, whereas methanol oxidation was generally
19 insensitive to step sites. By contrast, formic acid oxidation demonstrated reverse surface-
20 structure sensitivity. The negative slope indicated that the step sites were unfavorable for this
21 reaction, which is in agreement with the previous result of bulk Pd single crystal planes reported
22 by Hoshi and coworkers.³⁴
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40 **Reaction mechanism of the electrooxidation of formic acid and ethanol.** To further
41 understand the electrooxidation mechanism, density functional theory (DFT) calculations of
42 representative systems were carried out. According to the surface sensitivity (Figure 3C) and
43 structure characteristics of Pd NCs (Figure 2A), the oxidation of formic acid and ethanol on the
44 flat Pd(100) and stepped Pd(310) were modeled, and the main results are presented in Figure 4.
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52 For formic acid oxidation, the rate determining step (RDS) was found to be the decomposition
53 of adsorbed formate (HCOO*) via C-H bond breaking (Figure 4A). On the stepped Pd(310), the
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3 adsorption of HCOO^* is too strong for its decomposition, resulting in the step sites being
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5 poisoned by HCOO^* . The barrier of C-H bond breaking is 1.04 eV on Pd(310), which is higher
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7 than the value of 0.98 eV on Pd(100). Therefore, the oxidation rate on stepped Pd(310) should be
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9 slower than that on flat Pd(100). This result is consistent with the above experimental
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11 observation that step sites are unfavorable for formic oxidation (Figure 3).
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16 For the reaction mechanism of ethanol oxidation, adsorbed ethanol firstly breaks an α - C-H
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18 bond to form CH_3CHOH^* which reacts readily with surface OH^* to form acetaldehyde and
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20 water (Figure 4B). The acetaldehyde then dehydrogenates to form acetyl (CH_3CO^*) rapidly,
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22 which may continue to react following two competing processes. One is the partial oxidation
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24 process where CH_3CO^* is oxidized by surface OH^* to form acetate, and the other is the
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26 complete oxidation process where CH_3CO^* undergoes β -dehydrogenation to form CH_2CO^* , the
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28 latter then further reacts involving C-C bond breaking (broken line in Figure 4B). The partial
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30 oxidation path is energetically favorable on both flat Pd(100) and stepped Pd(310) surfaces.
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35 The RDS of partial oxidation of ethanol was found to be the cleavage of α - C-H bond to form
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37 CH_3CHOH^* . This was confirmed by our previous experimental result of high H/D kinetics
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39 isotope effect ($\text{KIE}=5.2$) for this step.³⁵ On the flat Pd(100), the effective barrier of α - C-H
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41 breaking is 1.17 eV, higher than 1.12 eV on the stepped Pd(310). This is related to higher
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43 binding energy of the adsorbate on step sites. Therefore the theoretical calculations predicted that
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45 step sites are favorable for ethanol oxidation, which is in fact in line with the experimental
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47 observation (Figure 3).
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52 Obviously the ethanol complete oxidation path is more desirable for direct ethanol fuel cell
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54 application as more electrons can be released per ethanol molecule, that is $12e^-$ in full oxidation
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3 instead of $4e^-$ in partial oxidation. The barrier of C-C bond breaking, $\text{CH}_2\text{CO}^* \rightarrow \text{CH}_2^* + \text{CO}^*$,
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5 is 0.97 eV on the flat Pd(100), whilst it decreases to 0.77 eV on the stepped Pd(310) (Figure 4B).
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7 Therefore it is evidenced that step sites will promote the C-C bond breaking, and such increase
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9 the selectivity to the full oxidation product CO_2 from ethanol oxidation. To verify this,
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11 electrochemical *in-situ* FTIR spectra of ethanol electrooxidation at 0.8 V (near peak potential) on
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13 Pd NCs of Cube{100}, THH{310} and THH{730} were collected and shown in Figure 5. The
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15 main product detected was acetate (IR absorption at around 1415 and 1553 cm^{-1} for the
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17 symmetric and asymmetric stretching band of COO, respectively). On the other hand, the IR
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19 band intensity of CO_2 (around 2343 cm^{-1}), the full oxidation product formed through C-C bond
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21 breaking, increased significantly as Pd NCs changed from cube to THH. The ratio of the IR band
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23 intensity of CO_2 to acetate (1415 cm^{-1}), denoted as η_{CO_2} , was used to evaluate the relative amount
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25 of full oxidation against the partial oxidation, i.e., the level of C-C bond breaking in the overall
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27 ethanol oxidation. The η_{CO_2} obtained from the highly stepped THH{730} was 1.7 and 7.0 times
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29 higher than those from the less stepped THH{310} and the flat Cube{100}, respectively. Clearly
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31 these *in-situ* FTIR data is in good agreement with the DFT calculations discussed above; and
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33 confirms that the stepped sites may facilitate ethanol C-C bond dissociation.
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41 **Comparison of electrocatalytic behaviors between Pd NCs and bulk Pd single-crystal**
42 **planes.** Polyhedral nanocrystals have not only facets, but also edges and 3D spatial structure.
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44 Crystal edges have very low coordinated atoms, and 3D spatial structure is relevant to local mass
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46 transfer, such as diffusion field of reactants near nanocrystals. Therefore, both the edges and the
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48 3D spatial structure are important for catalytic performance. The main advantage of the new
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50 model nanocatalyst proposed here over the traditional bulk single-crystal plane model catalysts is
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52 that the former can provide the reactivity information of edges and 3D spatial structure, relevant
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3 to real catalyst, but the latter cannot. To demonstrate this point, we carried out comparative
4 studies between Pd NCs and bulk Pd single-crystal planes with the same Miller indices.
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6 According to the surface structure sensitivity data shown in Figure 3C, ethanol electrooxidation
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8 on THH{310} Pd NCs and bulk Pd(310) single-crystal plane was selected as comparative study,
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10 under various ethanol concentrations and potential scan rates. Figure 6A shows cyclic
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12 voltammograms of ethanol oxidation on THH{310} Pd NCs and bulk Pd(310) single-crystal
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14 plane at 0.05 V s^{-1} in 1 M NaOH + 1 M ethanol. The catalytic activity of the bulk Pd(310) was
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16 2.2 times higher than that of THH{310} in view of peak current density. Analogous behavior
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18 could also be observed on bulk Pd(100) plane against Cube{100} Pd NCs (Figure S11). In
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20 addition, commercial Pd black catalyst exhibited voltammetric characteristics closer to Pd NCs
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22 than bulk Pd single-crystal planes (Figure S11). When ethanol concentration decreased, the
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24 difference in catalytic activity between bulk Pd single-crystal planes and Pd NCs was enlarged
25
26 sharply. For example, in 0.1 M ethanol solution, the ethanol oxidation current on Pd(310) was 19
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28 times higher than that on THH{310} (Figure 6B). Such a big difference challenges the reliability
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30 of using bulk single-crystal planes as model catalysts to explore the catalytic behaviors of
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32 nanocatalysts.
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41 Interestingly, it was found that the difference in catalytic activity between Pd NCs and bulk
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43 single-crystal planes was reduced as potential scan rate increased. We recorded the
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45 voltammograms in 1 M NaOH + 1 M ethanol at scan rate ranging from 0.02 to 10 V s^{-1} (Figure
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47 S12). The catalytic activity of THH{310} was close to that of Pd(310) at a very high scan rate of
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49 10 V s^{-1} (Figure 6C). Figure 6D depicts the ratio of the forward peak current density of Pd(310)
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51 to that of THH{310} (i.e., $j_{p,\text{Pd}(310)}/j_{p,\text{THH}\{310\}}$) as a function of the potential scan rate. The initial
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53 ratio was 2.8 at a very slow scan rate of 0.02 V s^{-1} , and gradually approached to one as the scan
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3 rate increased to 10 V s⁻¹. The similar scan rate dependence was also observed on commercial Pd
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5 black catalyst against Pd(310) (Figure S12).
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9 THH{310} Pd NCs and bulk Pd(310) plane have the same terrace-step atoms on facets/planes,
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11 but one of the main differences is that only the former contains low-coordinated edge sites
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13 (Figure 1). The electrooxidation of small organic molecules usually involves the dissociative
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15 adsorption to generate surface CO adsorbates, which can be strongly adsorbed on the surface and
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17 poison the catalysts.³⁶⁻³⁹ The dissociative adsorption of ethanol to form CO adsorbates involves
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19 the cleavage of strong C–H and C–C bonds, which may preferentially occur at highly active edge
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21 sites. Therefore, the electrochemical *in situ* FTIR spectra of ethanol oxidation on THH{310} and
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23 Pd(310) were collected at 0.45 V (close to the onset potential) where adsorbed CO was detected,
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25 see Figure 7A and 7B (red lines), respectively. The IR band at ~1820 cm⁻¹ is assigned to bridge-
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27 bonded CO (CO_B).^{37,38} To evaluate the adsorbed CO coverage, the FTIR spectra of saturated CO
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29 adsorption on the two surfaces were also collected (black lines) as references for monolayer CO
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31 adsorbates on the two surfaces. According to the relative intensity of the CO band generated
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33 from ethanol oxidation to that of the CO saturation adsorption, the CO_B coverage was estimated
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35 to be 0.088 and 0.017 for ethanol oxidation on THH{310} and Pd(310), respectively. Five times
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37 larger CO_B coverage obtained on THH{310} compared to that on Pd(310) indicates clearly that
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39 much more severe CO poisoning existed on THH{310} than that on Pd(310).
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47 It is well known that the proportion of edge sites on the NCs increases as particle size
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49 decreases (Figure S13). To investigate the correlation between CO poisoning and the amount of
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51 edge sites, we synthesized THH{310} Pd NCs with different sizes of 39, 77, and 113 nm (Figure
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53 S13) and studied ethanol oxidation on these samples, as well as the bulk Pd(310) and the
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55 commercial Pd black. The current–time curves of ethanol oxidation at 0.65 V on these catalysts
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3 were measured. Clearly, the decline rate of ethanol oxidation current increased with increasing
4 the proportion of edge sites, following the order of commercial Pd black > THH{310} (39 nm) >
5 THH{310} (77 nm) > THH{310} (113 nm) > bulk Pd(310) single-crystal plane (Figure 7C).
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10 This result suggests that the poisoning species are mainly produced on the edge sites.

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13 The proportion of edge sites on Pd NCs is very low (< 2%). If CO species generated at edge
14 sites were just fixed on edge sites, the catalytic activity of THH{310} should be close to that of
15 Pd(310). This is not consistent with the experimental observation. Severe poisoning on
16 THH{310} suggests that CO species generated at edge sites could diffuse to the facet sites,
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poison and deactivate them, as illustrated in Figure 7D.

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13 The generation of CO species on edge sites may also explain the dependence of the poisoning
14 effect on the scan rate and ethanol concentration shown in Figure 6. Generally, the dissociative
15 adsorption of small organic molecules on noble metal surfaces to produce CO species only
16 occurs at relatively low potentials and needs a few to tens of seconds for the accumulation of
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enough CO adsorbates that can poison the surfaces considerably.^{36, 37} As the scan rate increased,
the dwell time in the low-potential region was shortened, and the accumulated amount of CO
adsorbates decreased. For example, the dwell time at low potential was only tens of milliseconds
at 10 V s⁻¹, so that the accumulated CO species was negligible for such short time. Therefore, the
catalytic activity of THH{310} Pd NCs trended to bulk Pd(310) as the scan rate increased
(Figure 6D). The similar intrinsic activity observed on the two surfaces at a very high scan rate
also supports the fact that THH{310} and Pd(310) have similar plane/facet structures. This point
can help to exclude the possibility that the different catalytic activities observed in Figure 6A and
6B come from different plane/facet structures between THH{310} and Pd(310).

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3 The ethanol concentration effect is also related to the geometrical shape that determines the
4 local mass transfer. According to spherical diffusion model, mass transfer rate is inversely
5 proportional to radius of curvature of a particle. Crystal edges have a small radius of curvature,
6 and thus possess much higher mass transfer rate than facets/planes. When the ethanol
7 concentration decreased, mass transfer became more and more dominant, and edge sites
8 collected much more ethanol molecules than facet/plane sites. The poisoning effect on Pd NCs
9 became more severe in low-concentration ethanol solution. It is not unreasonable to observe that
10 the relative catalytic activity of Pd(310) against that of THH{310} increased from 2.2 to 19
11 when the ethanol concentration decreased from 1.0 to 0.1 M (Figure 6A and 6B).
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25 The above results demonstrated that the catalytic activity of bulk Pd(310) was much higher
26 than that of THH{310} for ethanol oxidation when potential scan rate or ethanol concentration
27 decreased. This difference was attributed to the edge sites which only exist on Pd NCs. The low-
28 coordinated edge sites promoted ethanol dissociation with C-C bond cleavage into poisoning CO
29 adsorbates that in turn diffused to the facets and suppressed the overall catalytic activity of Pd
30 NCs.
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40 CONCLUSIONS

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43 In summary, we have developed a model nanocatalyst based on well-defined surface structures
44 of Pd nanocrystals with continuously tunable $\{hk0\}$ high-index facets, and investigated the
45 structure–reactivity relationship of electrooxidation of a series of small organic molecules. It has
46 been found that Pd step sites are favorable for the oxidation of multi-carbon alcohols, but
47 unfavorable for formic acid oxidation. Pd nanocrystals and bulk Pd single-crystal planes with the
48 same Miller indices exhibited significantly different catalytic performance for ethanol oxidation,
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3 depending on potential scan rate and ethanol concentration. Such a difference was attributed to
4 the poisoning effects originating at Pd nanocrystal edge sites. The applications of this model
5 nanocatalyst will contribute to better understanding the structure–reactivity relationship properly
6 at the atomic and nanoscale level, and consequently to effectively realize the rational design of
7 high-performance catalysts.
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14 15 16 **EXPERIMENTAL SECTION**

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18 **Materials.** Palladium dichloride (PdCl_2 , 99.999%) and perchloric acid (HClO_4 , super pure)
19 were purchased from Alfa Aesar. Sodium hydroxide monohydrate ($\text{NaOH}\cdot\text{H}_2\text{O}$, 99.9995%) was
20 purchased from Sigma Aldrich. Methanol (MeOH), ethanol (EtOH), n-propanol (PrOH),
21 ethylene glycol (EG) and formic acid (HCOOH) were A.R. reagents and purchased from China
22 Medicine Shanghai Chemical Reagent Corp. The commercial Pd black catalyst was purchased
23 from Alfa Aesar (Johnson Matthey Inc.). All chemicals were used as received. The solutions
24 were prepared from super pure water ($18\text{ M}\Omega\text{ cm}$) purified through a Milli-Q Lab system
25 (Millipore Ltd.)
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33 **Preparation of Pd NCs.** Pd NCs were electrodeposited on a glassy carbon (GC, $\phi = 6\text{ mm}$) disk
34 electrode in $0.1\text{ mM PdCl}_2 + 0.1\text{ M HClO}_4$ solution in a standard three-electrode cell at room
35 temperature. The working electrode was the GC electrode. Prior to electrodeposition, the GC
36 electrode was polished mechanically by successively using alumina powder of sizes 5, 1, and $0.3\text{ }\mu\text{m}$,
37 and cleaned in an ultrasonic bath. The counter electrode was a Pd foil and reference
38 electrode was a saturated calomel electrode (SCE). All electrode potentials reported in this paper
39 were quoted versus the reverse hydrogen electrode (RHE) scale. Electrode potential was
40 controlled by PAR 263A potentiostat/galvanostat (EG&G) via a home-developed software that
41 could realize arbitrary potential waveform. The electrochemical square-wave potential (SWP)
42 method was applied to control the surface structure of Pd NCs. The SWP method contained the
43 following three stages: (1) The GC electrode was first subjected to a high potential of 1.5 V (vs.
44 RHE) and held for 4 s to clean the GC electrode; (2) The GC electrode was subjected to the
45 potential step from 1.50 V to a low potential of 0.10 V (E_N), and held for 40 ms to generate Pd
46 nuclei; (3) The growth of the Pd nuclei into Pd NCs was achieved by applying a SWP. The
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3 surface structure of Pd NCs can be tuned by changing the upper potential (E_U) of SWP from
4 0.950 to 1.040 V. The lower potential (E_L) of SWP was 0.600 V, and the frequency (f) was 100
5 Hz. The growth time was 45 min.
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9 **Characterization.** The morphology and structure of the as-synthesized Pd NCs were
10 characterized by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron
11 microscopy (TEM, JEM-2100 at 200 kV). Electrocatalytic activity of Pd nanocrystals was tested
12 by cyclic voltammetry. Prior to the test, the cyclic voltammograms (CVs) in 0.1 M HClO₄
13 solution was firstly recorded at 0.05 V s⁻¹, and the electroactive surface area of the Pd was
14 measured through the electric charge of hydrogen adsorption. The electrode was then transferred
15 to the solution containing small organic molecules including formic acid (HCOOH), methanol
16 (MeOH), ethanol (EtOH), n-propanol (PrOH), and ethylene glycol (EG), and stable CV was
17 recorded. The solution was 0.1 M HClO₄ + 0.1 M HCOOH or 1.0 M NaOH + 1.0 M
18 MeOH/EtOH/PrOH/EG. The current density was calculated through dividing the measured
19 current by the electroactive surface area. The reproducibility of electrocatalytic tests was fairly
20 good; for example, the relative standard deviation of peak current density recoded for ethanol
21 electrooxidation on six samples of THH{310} Pd NCs was about 8%.
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32 **Pd single-crystal electrodes.** Bulk Pd(100) and Pd(310) single-crystal planes were purchased
33 from MaTeck GmbH. Before each measurement, the Pd single-crystal electrodes were annealed
34 by induction heating under high-pure Ar atmosphere, and cooled also in Ar stream, and then
35 transferred to an electrochemical cell under the protection of a droplet of super pure water. The
36 annealed Pd single-crystal electrodes were characterized in N₂-purged 0.1 M HClO₄ solution by
37 cyclic voltammetry, and then transferred to 0.1 M HClO₄ + 0.1 M HCOOH or 1.0 M NaOH +
38 1.0 M ethanol for electrocatalytic tests. The oxidation current was normalized by geometric area
39 of the Pd electrodes to obtain the current density, since the roughness of annealed single-crystal
40 electrodes is close to 1.
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49 **Electrochemical *in situ* infrared spectroscopy.** *In situ* infrared spectroscopy was carried out
50 using a Nexus-870 FTIR spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A
51 detector and an EverGlo IR source. A thin-layer IR cell with a CaF₂ planar window was
52 employed. Infrared radiation sequentially passed through the CaF₂ window and the thin-layer
53 solution (~ 10 μm) between the window and the electrode surface, and then was reflected from
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3 the electrode surface. The resulting spectra were reported as relative change in reflectivity, that
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$$\frac{\Delta R}{R} = \frac{R(E_S) - R(E_R)}{R(E_R)}$$

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10 where $R(E_S)$ and $R(E_R)$ are the single-beam spectrum collected at sample potential (E_S) and
11 reference potential (E_R), respectively. As a result, for solution species, downward bands in the
12 resulting spectrum indicate the formation of products, while upward bands denote the
13 consumption of reactants. The spectral resolution was 8 cm^{-1} .
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17 **DFT computational methods.** The electronic structure calculations were performed using the
18 Vienna Ab-initio Simulation Package (VASP), using Perdew-Burke-Ernzerh (PBE) generalized
19 gradient approximation (GGA) exchange-correlation functional. The projector-augmented-wave
20 (PAW) pseudopotentials were utilized to describe the core electron interaction.⁴⁰⁻⁴⁴ Considering
21 the structure characteristics of Pd NCs, both the flat Pd(100) and stepped Pd(310) were modeled.
22 The 4-layer close-packed Pd(100) and Pd(310) slabs were built with 24 atoms. The vacuum
23 region layers were built more than 12 \AA . The cut-off energy was 400 eV and a $3 \times 3 \times 1$
24 Monkhorst-Pack k -point sampling was used for two-dimensional Brillouin integrations. During
25 all the optimization processes, the bottom half atoms were fixed in the slab while the top half
26 atoms were relaxed. The transition states were located with a constrained method with the
27 converge criteria of the force below 0.05 eV/\AA .⁴⁵ The reaction free energy (ΔG) was calculated
28 as the $\Delta G = \Delta E - T\Delta S$, where ΔE denotes the reaction energy, and ΔS is the entropy change
29 during the adsorption or desorption on the surface ($T = 300\text{K}$).
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44 ASSOCIATED CONTENT

45 **Supporting Information.** Supplement SEM and TEM images of Pd nanocrystals and cyclic
46 voltammograms of ethanol oxidation. This material is available free of charge via the Internet at
47 <http://pubs.acs.org>.
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Notes

The authors declare no competing financial interest.

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Figures

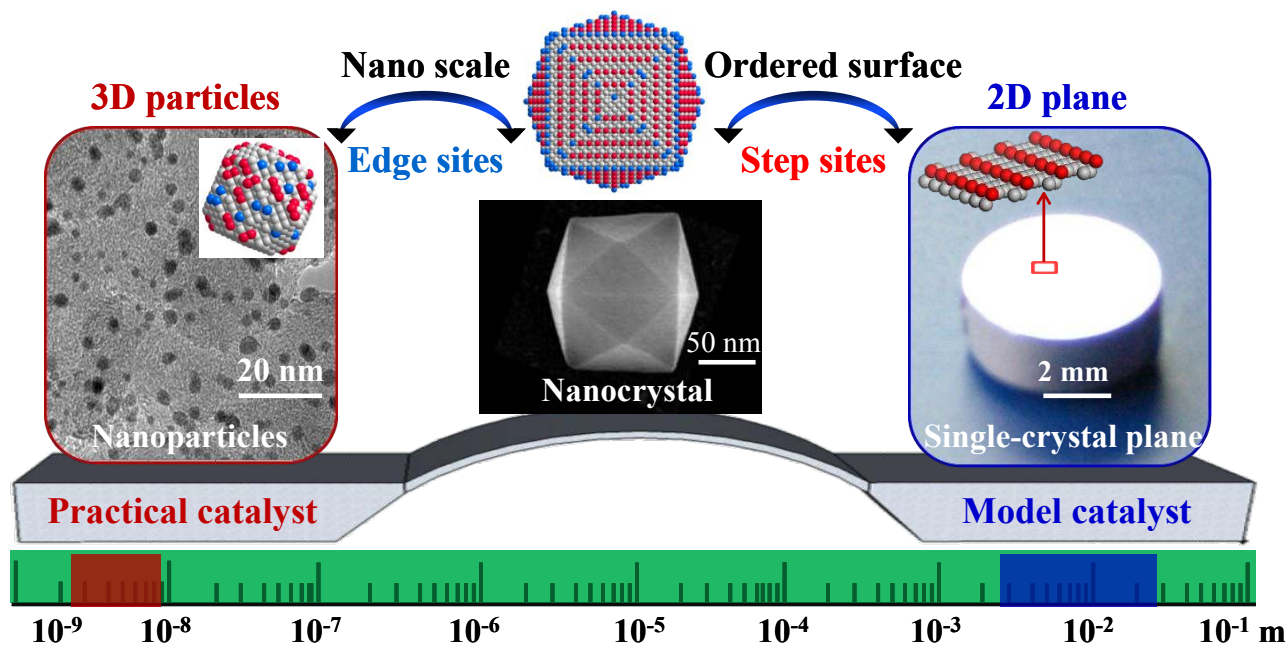


Figure 1. Illustration of the principle of continuously tunable nanocrystals to bridge the gap between model catalysts of single-crystal planes and practical catalysts. Practical catalysts consist of 3D nanoparticles with complex surface structures, whilst traditional model catalysts are macro-sized 2D single-crystal planes with ordered structure. Nanocrystals synthesized in this study have tunable and ordered facets as single-crystal planes, and edge sites as those on practical catalysts, thus they can serve as a new model catalyst to bridge the gap between model catalysts of single-crystal planes and practical catalysts.

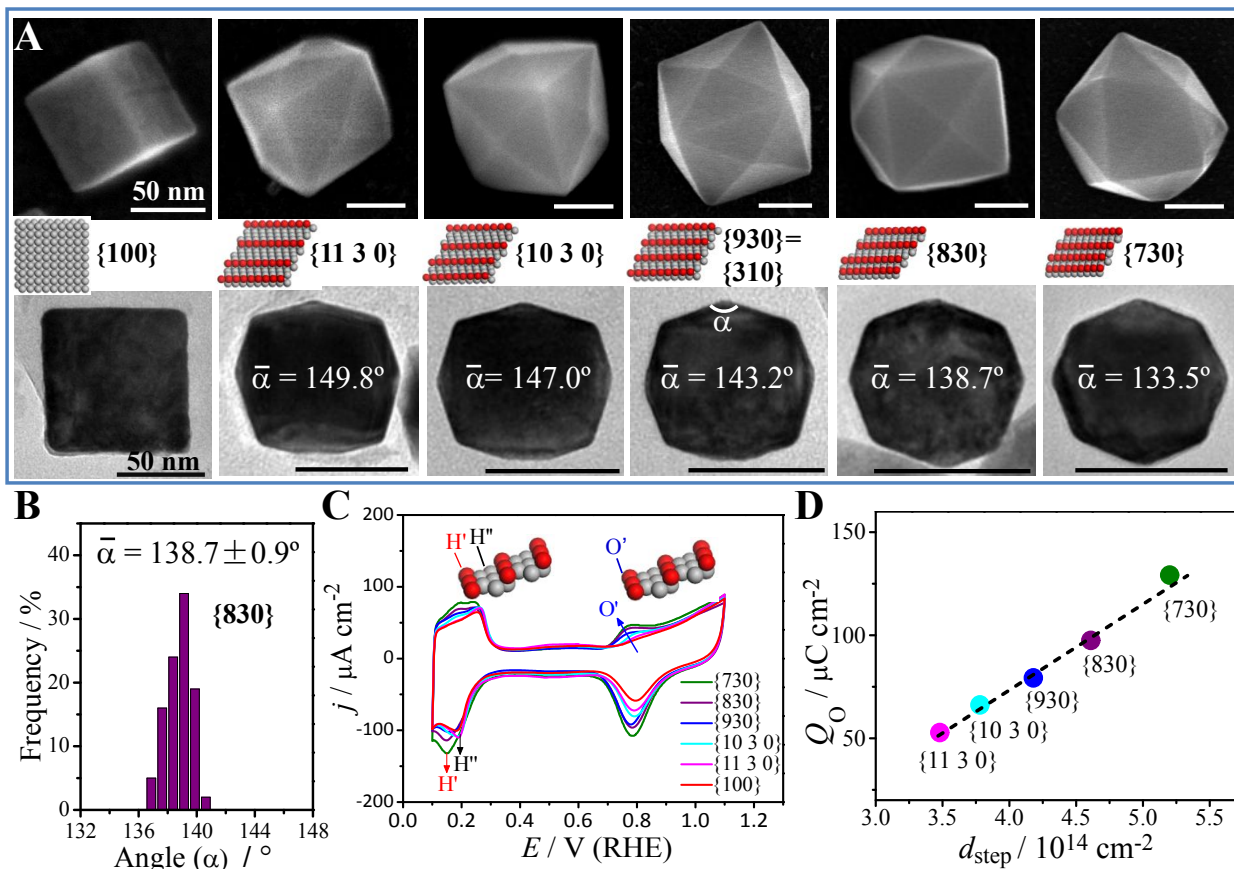


Figure 2. (A) SEM and TEM images of Pd NCs prepared by electrochemical square-wave potential method with different upper limit potential (E_U) in 0.1 mM PdCl₂ + 0.1 M HClO₄. The scale bars represent 50 nm. Pd nanocubes were obtained at $E_U = 0.950$ V; THH Pd NCs with {11 3 0}, {10 3 0}, {930}, {830} and {730} facets were obtained at E_U of 1.000, 1.010, 1.020, 1.030 and 1.040 V, respectively. The atomic models of these facets are also illustrated. (B) Histogram of the interfacial angle α of THH{830} Pd NCs. (C) Cyclic voltammograms of the Pd NCs recorded in 0.1 M HClO₄ solution, scan rate: 0.05 V s⁻¹. (D) Integral charge density (Q_O) associated with oxygen-species adsorption on the step sites of THH Pd NCs between 0.700 to 0.900 V as a function of the calculated density of step sites.

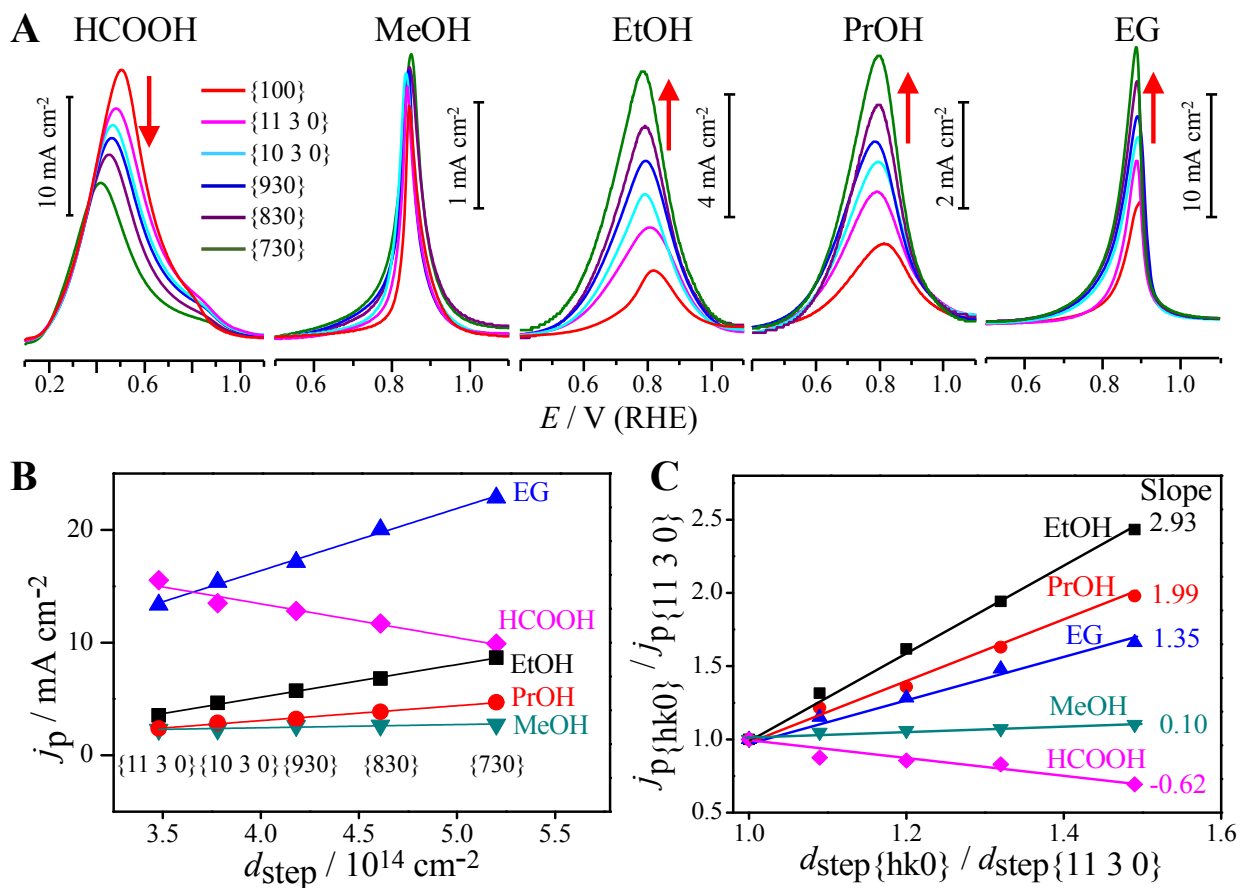


Figure 3. (A) Linear sweep voltammograms of electrooxidation of formic acid (HCOOH), methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), and ethylene glycol (EG) on the Pd NCs. The solution was 0.1 M HClO₄ + 0.1 M HCOOH or 1.0 M NaOH + 1.0 M MeOH/EtOH/PrOH/EG. Scan rate: 0.05 V s⁻¹. (B) The dependence of peak current density on the density of step sites. (C) Normalized peak current density vs. normalized density of step sites using the values of THH{11 3 0} as reference. The slopes reflect the surface-structure sensitivity of the reactions.

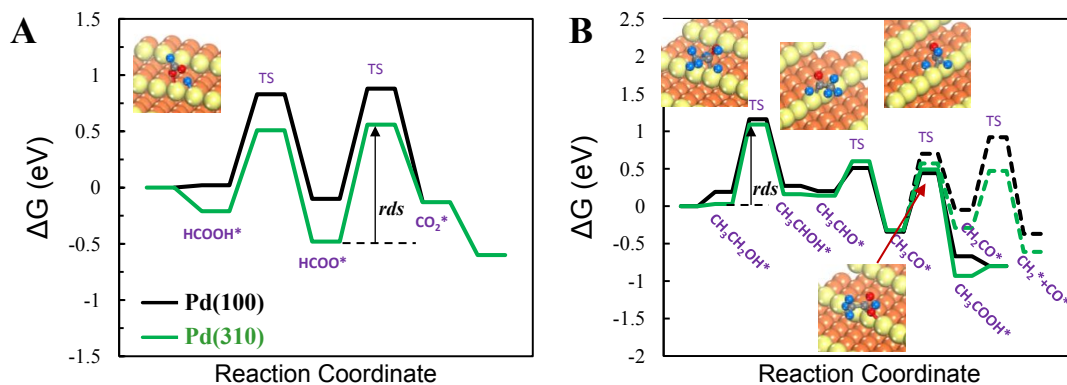


Figure 4. Free energy profiles for the oxidation of formic acid (A) and ethanol (B) on the flat Pd(100) and stepped Pd(310) planes. Black line is for Pd(100) plane and green line for Pd(310) plane. The broken line in (B) is for the complete oxidative reaction process of ethanol involving the C-C bond breaking. Insets are the key located transition states on Pd(310). Brown and yellow balls represent Pd on terrace and step sites, respectively; blue balls: H; grey balls: C; red balls: O.

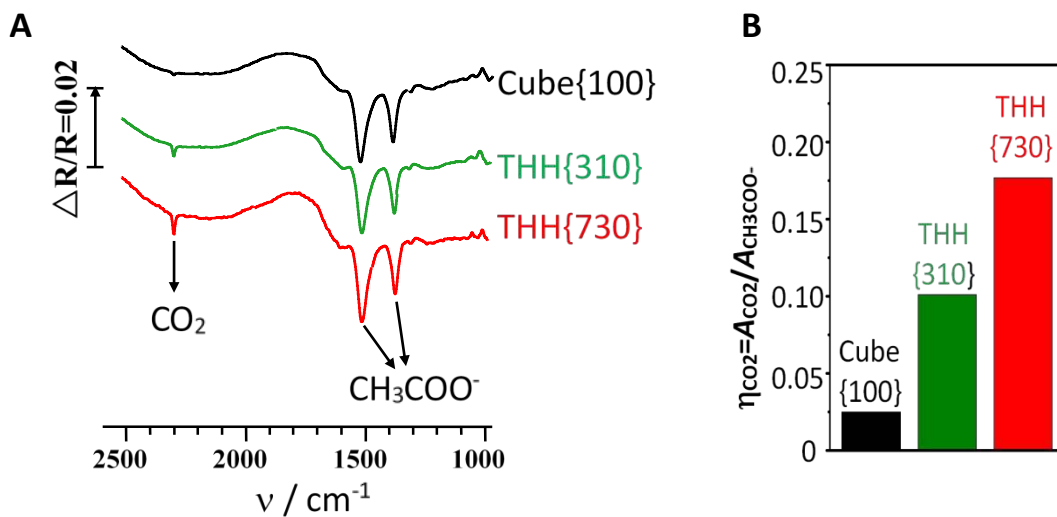


Figure 5. (A) *In situ* FTIR spectra of ethanol oxidation on Pd NCs of Cube{100}, THH{310}, and THH{730} in 1.0 M ethanol + 0.1 M NaOH solution. Sample potential $E_S = 0.8$ V; reference potential $E_R = 0.1$ V. (B) The ratio of IR band intensities (peak area) of CO_2 at around 2343 cm^{-1} to acetate at around 1415 cm^{-1} .

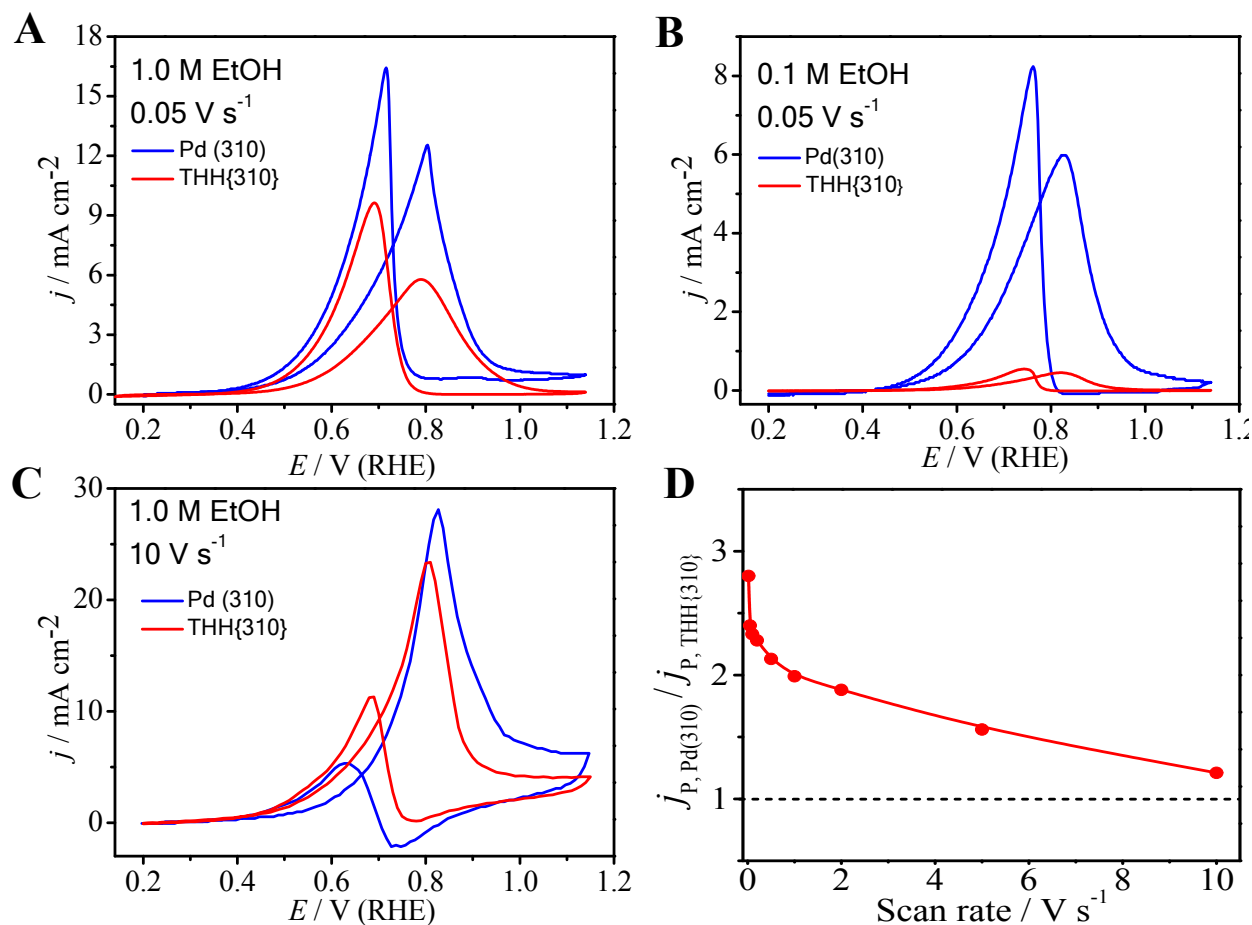


Figure 6. Cyclic voltammograms of ethanol electrooxidation on THH{310} and Pd(310) in (A) 1.0 M ethanol + 1.0 M NaOH at 0.05 V s⁻¹; (B) 0.1 M ethanol + 1.0 M NaOH at 0.05 V s⁻¹; (C) 1.0 M ethanol + 1.0 M NaOH at 10 V s⁻¹. (D) The ratio of the forward peak current density of ethanol oxidation on Pd(310) to that on THH{310} as a function of potential scan rate varying from 0.02 to 10 V s⁻¹, same ethanol solution as in (C).

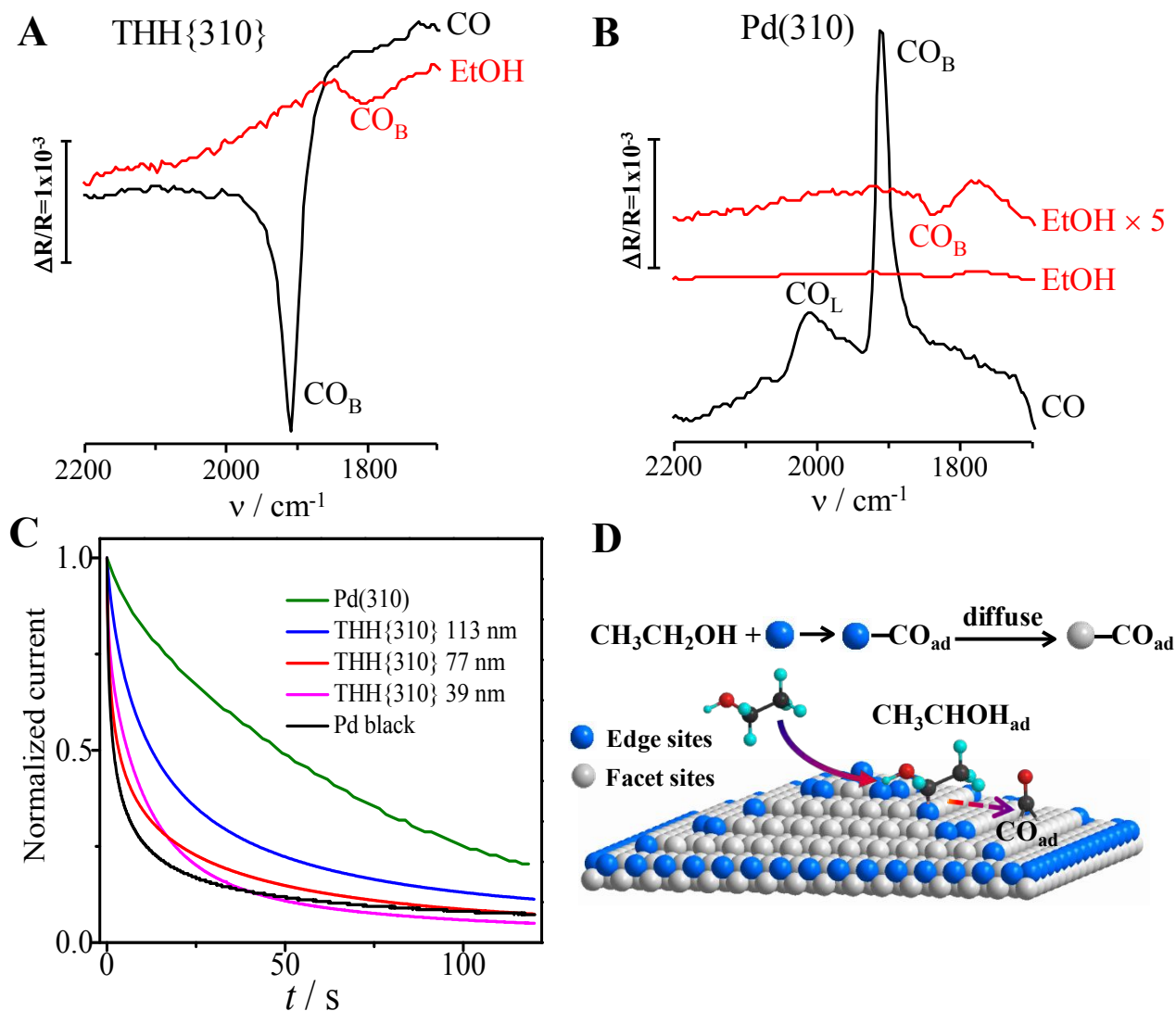


Figure 7. (A, B) Electrochemical *in situ* FTIR spectra of the CO adsorbates generated from the dissociative adsorption of ethanol (red lines) on THH{310} Pd NCs (A) and bulk Pd(310) surface (B) in 1 M NaOH + 1 M ethanol (sample potential $E_S = 0.45$ V, reference potential $E_R = 0.25$ V) and the saturated monolayer CO adsorbate (black lines) in 1 M NaOH ($E_S = 0.85$ V, $E_R = 0.25$ V). The spectrum of the CO generated from ethanol on bulk Pd(310) enlarged by 5 times was also shown in B for clarity. (C) Normalized current–time curves for ethanol oxidation on THH{310} Pd NCs of different sizes, bulk Pd(310), and commercial Pd black catalyst at 0.65 V in 1.0 M ethanol + 1.0 M NaOH. (D) Illustration of CO poisoning effect of THH Pd NCs. Edge sites promote ethanol dissociation to produce poisoning CO adsorbates that diffuse to the facets and deactivate them.

Supporting Information for

Pd nanocrystals with continuously tunable high-index facets as a model nanocatalyst

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1. Analysis of surface structure of tetrahexahedral Pd nanocrystals (THH Pd NCs)

A tetrahexahedron can be seen as a cube with each face capped by a square-based pyramid, and has 24 $\{hk0\}$ high-index facets. The Miller indices of the facets on a THH NC of face-centered cubic metals depend on its geometric parameters, such as the interfacial angle (α) or the ratio of the height of square-based pyramid to the edge length of cube (b/a), as illustrated in Figure S1. The facets are best revealed by imaging the THH NC along $[001]$, parallel to which 8 of the 24 facets are observed edge-on. The Miller indices can be determined through measuring the interfacial angles α .

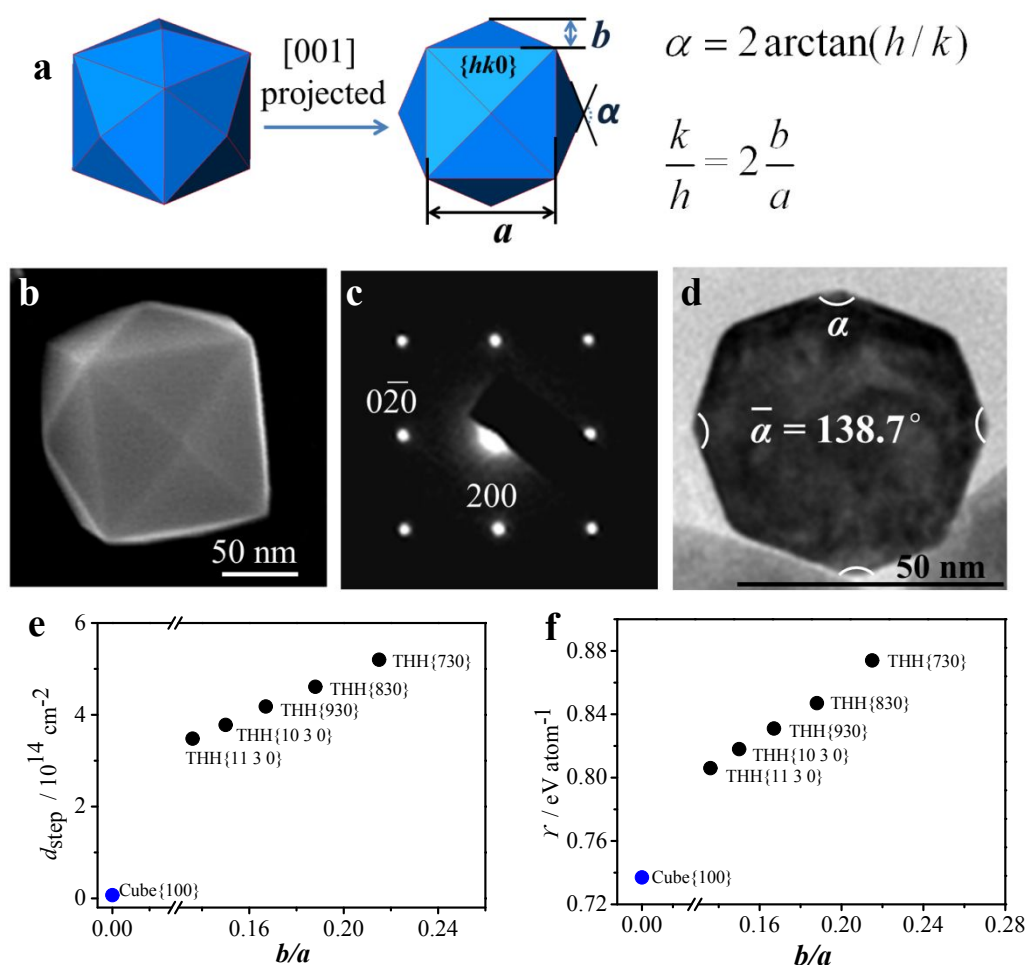


Figure S1. (a) Model of THH NC viewed from near $[111]$ direction and $[001]$ direction. (b) SEM image of a THH Pd NC. (c) Selected-area electron diffraction (SAED) pattern of a THH Pd NC along $[001]$ direction. (d) TEM image of the THH Pd NC recorded along $[001]$ direction. (e) Variation of the density of step sites against the structure parameter of b/a of THH Pd NCs. (f) Variation of the surface energy against b/a .

The interfacial angle α was measured to be 138.7° , which is close to the theoretical value of 138.9° on a THH NC enclosed by $\{830\}$ facets (see table S1).

When the geometric parameters (such as angle α and the value of b/a) of THH Pd NCs change, the Miller indices of facets, the density of step sites (d_{step}) and the surface energy will vary accordingly, as listed in Table S1. That is, the surface structure of THH Pd NCs is adjustable. As illustrated in Figure S1e and S1f, the d_{step} and surface energy approximately increase linearly with the value of b/a in the Miller indices ranging from $\{11\ 3\ 0\}$ to $\{730\}$. It is well known that the surface energy plays a key role in surface structure-controlled synthesis of metal NCs, because NCs growth tends to the lowest total surface energy. Clearly, THH Pd NCs enclosed by $\{hk0\}$ high-index facets possess much higher surface energy than the cubic Pd NCs bounded with $\{100\}$ facets. In addition, the difference in surface energy of vicinal $\{hk0\}$ high-index facets is very small, only about 10 milli-eV atom⁻¹ (Table S1). Such a small difference in the energy level leads to a great difficulty in achieving continuously tunable $\{hk0\}$ high-index facets of THH Pd NCs.

Table S1. Theoretical values of the interfacial angle (α), the ratio of the height of square-based pyramid to the edge length of cube (b/a), Miller indices, the density of step sites (d_{step}) and the surface energy of different $\{hk0\}$ facets on THH Pd NCs.

α	b/a	Miller indices	$d_{\text{step}} / 10^{14} \text{ cm}^{-2}$	Surface energy / eV atom ⁻¹
/	0	$\{100\}$	/	0.737
149.5°	0.136	$\{11\ 3\ 0\}$	3.48	0.806
146.6°	0.150	$\{10\ 3\ 0\}$	3.78	0.818
143.1°	0.167	$\{930\}=\{310\}$	4.18	0.831
138.9°	0.188	$\{830\}$	4.61	0.847
133.6°	0.214	$\{730\}$	5.20	0.874

2. Characterization of Pd NCs with continuously tunable surface structures

2.1 Pd nanocubes enclosed by {100} facets (Cube {100})

Pd nanocubes of {100} facets were obtained at $E_U = 0.950$ V. Figure S2 shows the SEM and TEM characterizations of them. Statistical analysis indicates that the yield of cubic morphology of Pd NCs reaches as high as 90%, and the average size of the Pd nanocubes is 76 ± 12 nm.

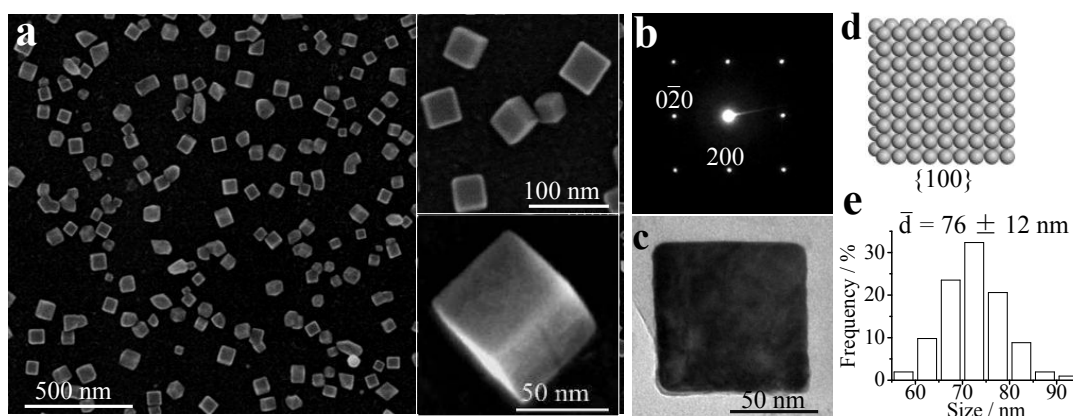


Figure S2. Morphology and structure characterization of Pd nanocubes. The electrochemical synthesis was conducted at $E_N = 0.100$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 0.950$ V, $f = 100$ Hz, and with growth time $t_{\text{growth}} = 45$ min, in 0.1 mM PdCl₂ + 0.1 M HClO₄ solution. (a) SEM image of Pd nanocubes, the insets are the high-magnification SEM images of the Pd nanocubes; (b) SAED pattern of a Pd nanocube along [001] direction; (c) TEM image of the Pd nanocube along [001] direction; (d) Model of atomic arrangement of {100} facets; (e) Histogram of size distribution of the Pd nanocubes.

2.2 THH Pd NCs enclosed by {11 3 0} facets (THH{11 3 0})

THH Pd NCs of {11 3 0} facets were obtained at $E_U = 1.000$ V. Figure S3 shows the SEM and TEM characterizations of them. Statistical analysis indicates that the yield of THH morphology of Pd NCs exceeds 90%, and the average size is 80 ± 14 nm. The average value of interfacial angle α on the THH Pd NCs is measured to be 149.9° , which is very close to the theoretical value of $\alpha = 149.5^\circ$ on a THH NC enclosed by {11 3 0} facets. The atomic arrangement of the Pd{11 3 0} surface is periodically composed of two {410} subfacets followed by one {310} subfacet, and the density of step sites is $3.48 \times 10^{14} \text{ cm}^{-2}$.

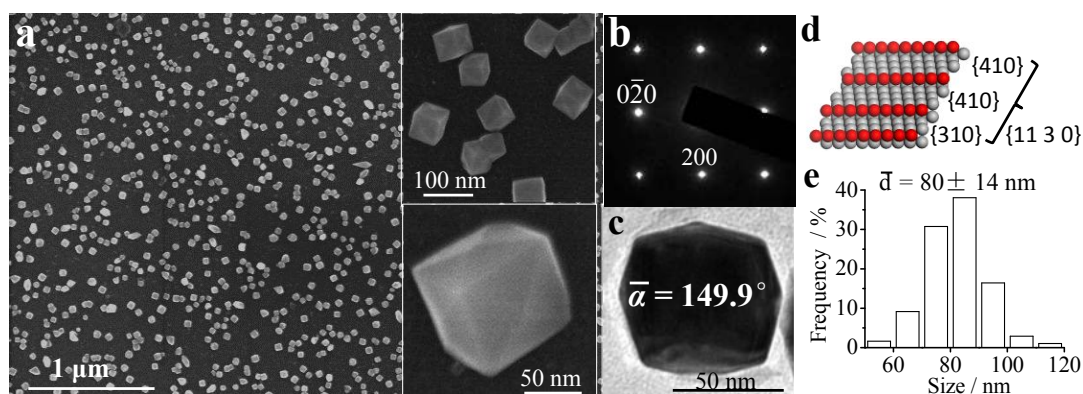


Figure S3. Morphology and structure characterization of THH{11 3 0} Pd NCs. The electrochemical synthesis was conducted at $E_N = 0.100$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 1.000$ V, $f = 100$ Hz, and with growth time $t_{\text{growth}} = 45$ min, in 0.1 mM PdCl₂ + 0.1 M HClO₄ solution. (a) SEM image of THH Pd NCs, the insets are the high-magnification SEM images of the THH Pd NCs; (b) SAED pattern of a THH Pd NC along [001] direction; (c) TEM image of the THH Pd NC along [001] direction; (d) Model of atomic arrangement of {11 3 0} plane; (e) Histogram of size distribution of the THH{11 3 0}.

2.3 THH Pd NCs enclosed by $\{10\ 3\ 0\}$ facets (THH $\{10\ 3\ 0\}$)

THH Pd NCs of $\{10\ 3\ 0\}$ facets were obtained at $E_U = 1.010$ V. Figure S4 shows the SEM and TEM characterizations of them. The average size is 79 ± 15 nm. The average value of interfacial angle α on the THH Pd NCs is measured to be 147.0° , which is close to the theoretical value of $\alpha = 146.6^\circ$ on a THH NC enclosed by $\{10\ 3\ 0\}$ facets. The atomic arrangement of the Pd $\{10\ 3\ 0\}$ surface is periodically composed of two $\{310\}$ subfacets followed by one $\{410\}$ subfacet, and the density of step sites is 3.78×10^{14} cm $^{-2}$.

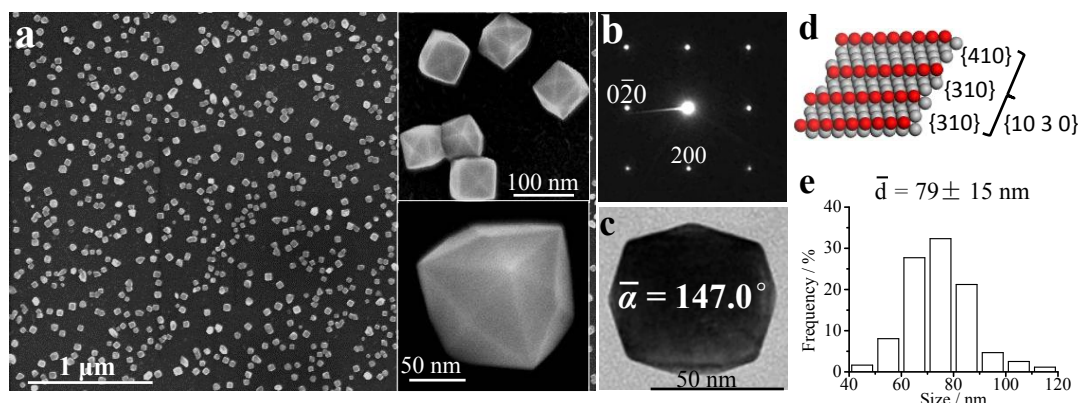


Figure S4. Morphology and structure characterization of THH $\{10\ 3\ 0\}$ Pd NCs. The electrochemical synthesis was conducted at $E_N = 0.100$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 1.010$ V, $f = 100$ Hz, and with growth time $t_{\text{growth}} = 45$ min, in 0.1 mM PdCl $_2$ + 0.1 M HClO $_4$ solution. (a) SEM image of THH Pd NCs, the insets are the high-magnification SEM images of the THH Pd NCs; (b) SAED pattern recorded by rotating the THH Pd NC to $[001]$ direction; (c) TEM image of the THH Pd NC along $[001]$ direction; (d) Model of atomic arrangement of $\{10\ 3\ 0\}$ plane; (e) Histogram of size distribution of the THH $\{10\ 3\ 0\}$.

2.4 THH Pd NCs enclosed by {930} facets (THH{930})

The {930} facet is equal to {310} facet. THH Pd NCs of {930} facets were obtained at $E_U = 1.020$ V. Figure S5 shows the SEM and TEM characterizations of them. The average size is 77 ± 14 nm. The average value of interfacial angle α on the THH Pd NCs is measured to be 143.2° , which is very close to the theoretical value of $\alpha = 143.1^\circ$ on a THH NC enclosed by {930} facets. The density of step sites on {930} is $4.18 \times 10^{14} \text{ cm}^{-2}$.

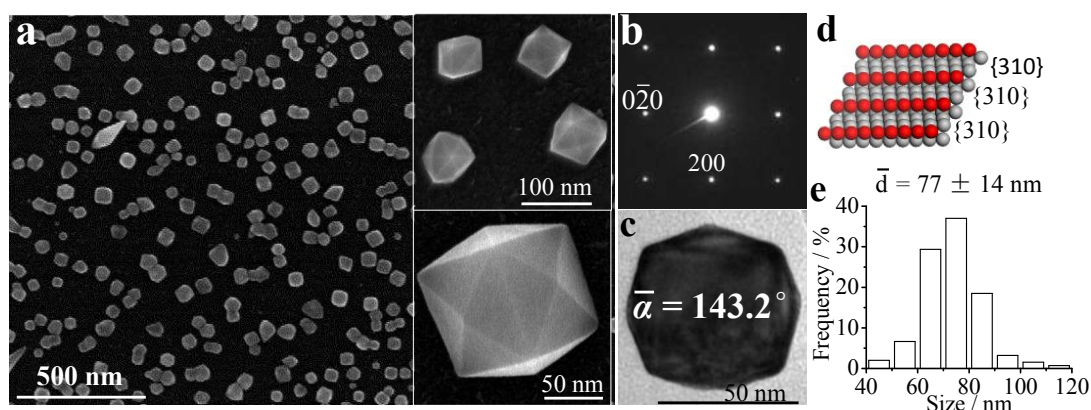


Figure S5. Morphology and structure characterization of THH{930} Pd NCs. The electrochemical synthesis was conducted at $E_N = 0.100$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 1.020$ V, $f = 100$ Hz, and with growth time $t_{\text{growth}} = 45$ min, in $0.1 \text{ mM PdCl}_2 + 0.1 \text{ M HClO}_4$ solution. (a) SEM image of THH Pd NCs, the insets are the high-magnification SEM images of the THH Pd NCs; (b) SAED pattern recorded by rotating the THH Pd NC to [001] direction; (c) TEM image of the THH Pd NC along [001] direction; (d) Model of atomic arrangement of {930} plane; (e) Histogram of size distribution of the THH{930}.

2.5 THH Pd NCs enclosed by {830} facets (THH{830})

THH Pd NCs of {830} facets were obtained at $E_U = 1.030$ V. Figure S6 shows the SEM and TEM characterizations of them. The average size is 76 ± 15 nm. The average value of interfacial angle α on the THH Pd NCs is measured to be 138.7° , which is close to the theoretical value of $\alpha = 138.9^\circ$ on a THH NC enclosed by {830} facets. The atomic arrangement of the Pd {830} surface is periodically composed of two {310} subfacets followed by one {210} subfacet, and the density of step sites is 4.61×10^{14} cm⁻².

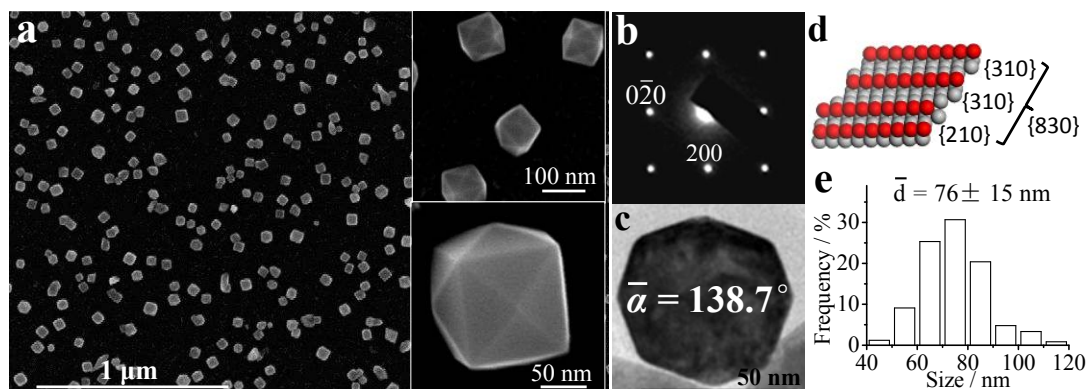


Figure S6. Morphology and structure characterization of THH{830} Pd NCs. The electrochemical synthesis was conducted at $E_N = 0.100$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 1.030$ V, $f = 100$ Hz, $t_{\text{growth}} = 45$ min, and in 0.1 mM PdCl₂ + 0.1 M HClO₄ solution. (a) SEM images of THH Pd NCs, the insets are the high-magnification SEM images of the THH Pd NCs; (b) SAED pattern recorded by rotating the THH Pd NC to [001] direction; (c) TEM image recorded with the THH Pd NC along [001] direction; (d) Model of atomic arrangement of {830} plane; (e) Histogram of size distribution of the THH{830}.

2.6 THH Pd NCs enclosed by {730} facets (THH{730})

THH Pd NCs of {730} facets were obtained at $E_U = 1.040$ V. Figure S7 shows the SEM and TEM characterizations of them. The average size is 78 ± 15 nm. The average value of interfacial angle α on the THH Pd NCs is measured to be 133.6° , which is very close to the theoretical value of $\alpha = 133.6^\circ$ on a THH NC enclosed by {730} facets. The atomic arrangement of the Pd{730} surface is periodically composed of two {210} subfacets followed by one {310} subfacet, and the density of step sites is 5.20×10^{14} cm $^{-2}$.

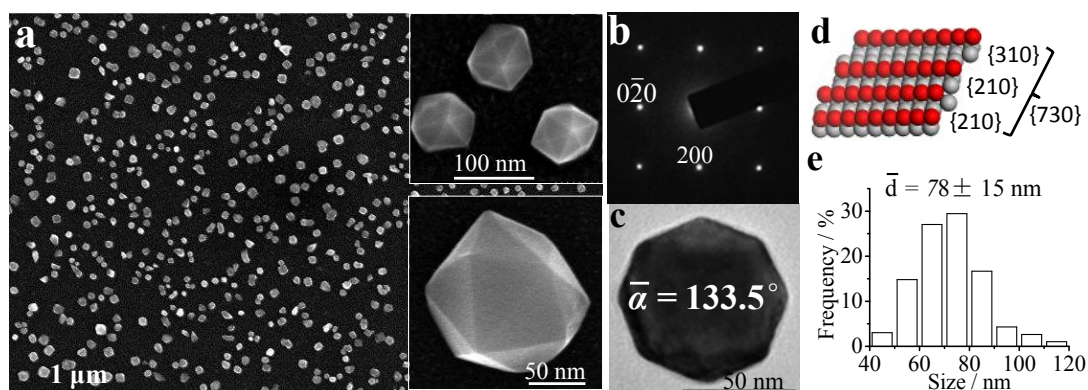


Figure S7. Morphology and structure characterization of THH{730} Pd NCs. The electrochemical synthesis was conducted at $E_N = 0.100$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 1.040$ V, $f = 100$ Hz, and with growth time $t_{\text{growth}} = 45$ min, in 0.1 mM PdCl $_2$ + 0.1 M HClO $_4$ solution. (a) SEM image of THH Pd NCs, the insets are the high-magnification SEM images of the THH Pd NCs; (b) SAED pattern recorded by rotating the THH Pd NC to [001] direction; (c) TEM image of the THH Pd NC along [001] direction; (d) Model of atomic arrangement of {730} plane; (e) Histogram of size distribution of the THH{730}.

2.7 The distribution of interfacial angle (α) of THH Pd NCs

To reveal the uniformity of the facets, we captured TEM images of over 20 THH Pd NCs along [001] direction and measured the interfacial angle of α . Figure S8 shows the TEM images of {830}-faceted THH Pd NCs. The result indicates that the average value of interfacial angle α is 138.7° , and the deviation is as small as 0.9° , which is essentially the same with the angle deviation (about $\pm 1^\circ$) of bulk single-crystal planes during the orientation and cutting.

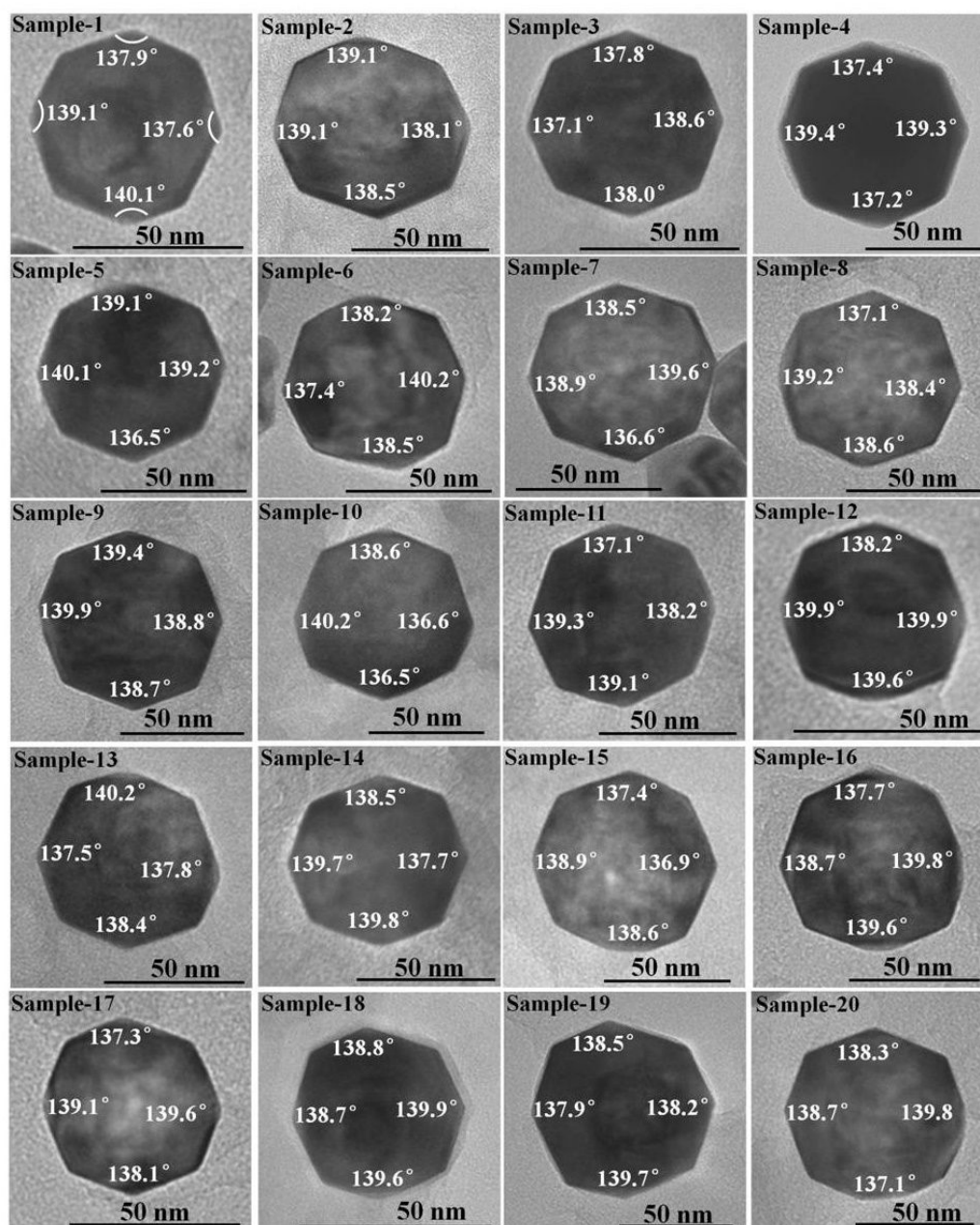


Figure S8. Some representative TEM images of THH{830} Pd NCs for the statistics of the distribution of interfacial angle α . All TEM images of the THH Pd NCs were recorded along [001] direction.

3. Electrochemical stability of Pd NCs with high-index facets

High-index facets were formed under the very harsh electrochemical conditions consisting of repeated oxidation–reduction cycling induced by square-wave potential, so it is expected that THH Pd NCs have high resistance against electrochemical corrosion. To verify it, we carried out a stability test of THH{830} Pd NCs by applying 5000 potential cycles between 0.1 and 1.1 V (vs RHE) at 0.05 V s⁻¹ in 0.1 M HClO₄. As shown in Figure S9, the cyclic voltammogram of THH{830} changed little after the 5000 potential cycles. The peak current of hydrogen and oxygen adsorption/desorption only decreased by 0.4% and 0.2%, respectively, after the 5000 potential cycles. Moreover, the SEM and TEM data shows that Pd NCs still maintained perfect THH shape with the {830} surface facet after the stability test. The interfacial angle (α) was very close to the theoretical of 138.9° for {830}-faceted THH NC. These experimental results demonstrated that the surface structure of THH Pd NCs was very stable under applied potential at the normal electrochemical conditions.

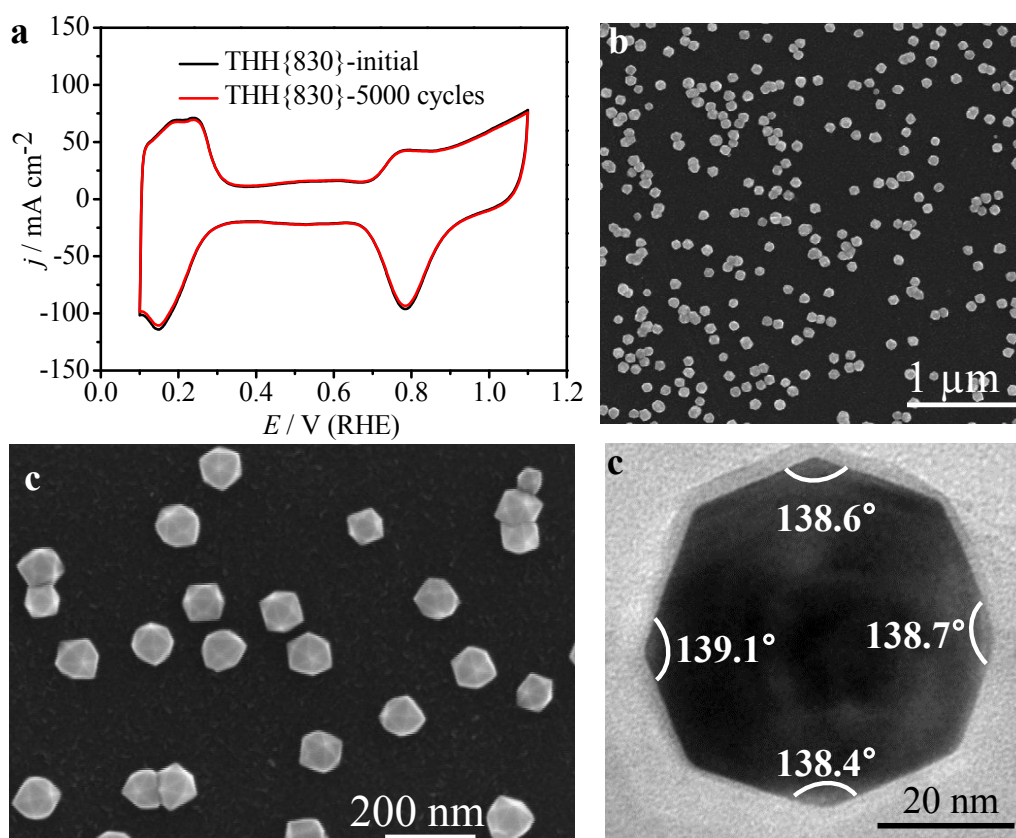


Figure S9. (a) Cyclic voltammograms of THH{830} Pd NCs in 0.1 M HClO₄ before and after a stability test by applying 5000 potential cycles between 0.1 and 1.1 V (vs RHE) at 0.05 V s⁻¹. (b, c) Low- and high-magnification SEM and (d) TEM images of THH{830} Pd NCs after the stability test.

4. CO stripping on Pd NCs

CO is widely used as a probe molecule to study surface structure and properties. We tested the CO stripping on the Pd NCs with different crystal faces, as shown in the Figure S10. The peak potentials of CO oxidation shifted positively with increasing the density of step sites (d_{step}). The low-coordinated step sites may facilitate the adsorption of both CO and the surface O/OH formed from water dissociative adsorption. The former is unfavorable for CO oxidation, while the latter is favorable for the oxidation reaction. The positively shifting of CO stripping peak potential with increasing step sites may indicate that the strength of the CO adsorption dominates the oxidation reaction, the latter is very sensitive to the surface structure and is consistent with the continuous change of the surface structure from $\{100\}$ to $\{730\}$ facets. Such relationship between CO stripping peak potential and the density of step sites also confirms the variation of surface structure of Pd NCs.

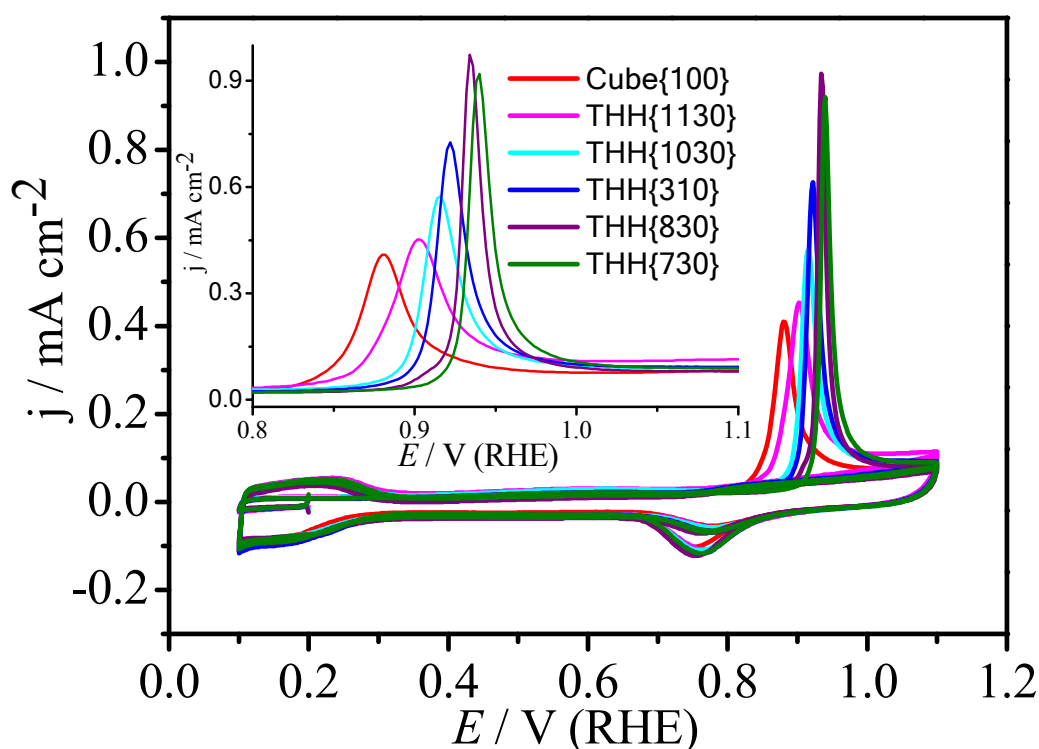


Figure S10. CO stripping voltammograms recorded on a series of Pd NCs in 0.1M HClO₄ solution. Scan rate: 0.05 V s⁻¹. CO was pre-adsorbed at the lower potential region then the solution CO was removed by N₂ purge for 20 min before the stripping tests. The inset shows the magnified voltammograms near the oxidation peak potential.

5. Electrochemical behaviors of Pd catalysts

5.1 Comparison of catalytic activity of different Pd catalysts for ethanol oxidation

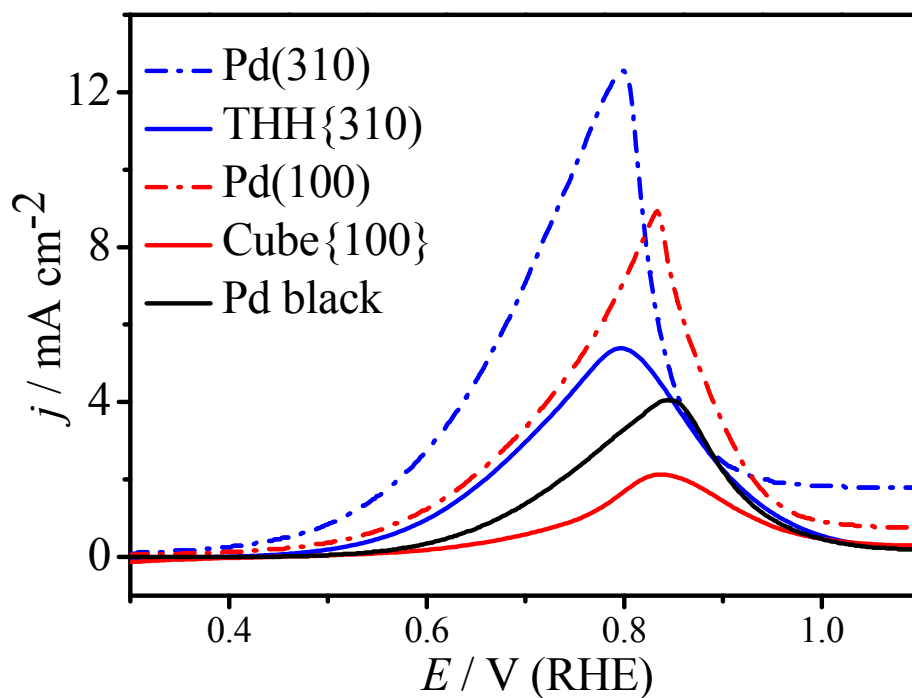


Figure S11. Comparison of voltammograms of ethanol electrooxidation on bulk Pd(310) and Pd(100) planes, Pd NCs of THH{310} and Cube{100}, as well as a commercial Pd black catalyst. The solution: 1.0 M $\text{CH}_3\text{CH}_2\text{OH}$ + 1.0 M NaOH; scan rate: 0.05 V s^{-1} .

5.2 Dependence of scan rate on the electrocatalytic activity of different Pd catalysts

Figure S12 illustrates the CVs of ethanol oxidation on Pd(310), THH{310}, and commercial Pd black at different scan rates ranging from 0.02 to 10 V s⁻¹. At low scan rate (< 1 V s⁻¹), the j_p of Pd(310) is much larger than those of THH{310} and Pd black. At high scan rate, the j_p on different catalysts tends to similar.

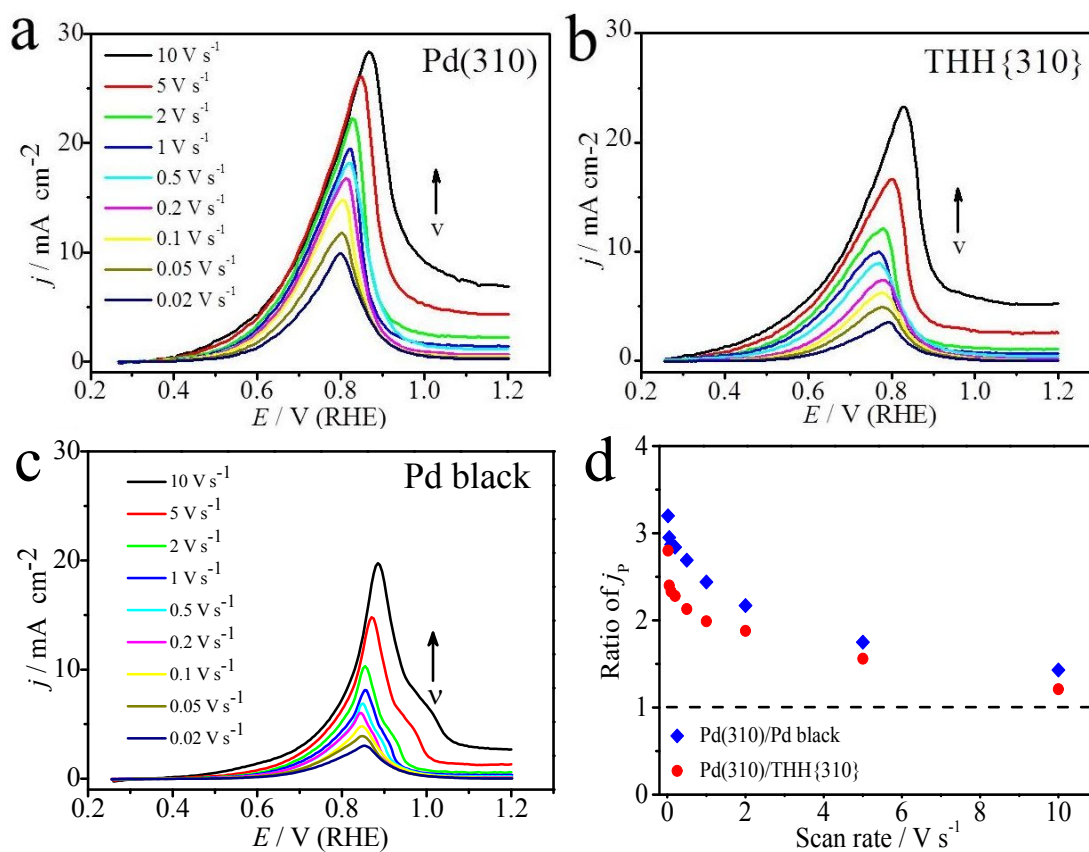


Figure S12. Effect of potential scan rate on the j_p of ethanol oxidation. The forward voltammograms of ethanol oxidation on (a) Pd(310), (b) THH{310}, and (c) commercial Pd black catalyst in 1.0 M CH₃CH₂OH + 1.0 NaOH at different scan rates. (d) The ratio of peak current density of Pd(310) to THH{310} and Pd black as a function of potential scan rate.

6. THH{310} Pd NCs with different sizes

The ratio of edge atoms to total surface atoms increases with decreasing particles size. To further understand the role of edge atoms played in catalytic reaction, we synthesized THH Pd NCs of {310} facets with different size. Figure S13a-c show SEM images and size histogram of THH{310} with sizes of 39, 77 and 113 nm. Figure S13d depicts the percentage of edge atoms as a function of particle size. When the size of THH{310} is larger than 80 nm, the ratio of edge atoms to total surface atom is extremely small, less than 1%.

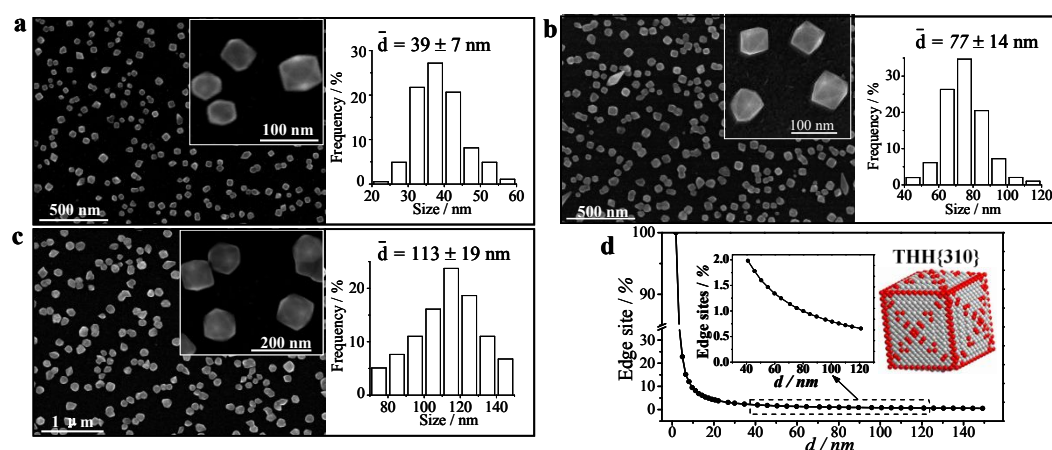


Figure S13. SEM of THH{310} Pd NCs with different sizes and size distribution. THH Pd NCs synthesized at $E_N = 0.100$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 1.020$ V, $f = 100$ Hz, in 0.1 mM PdCl₂ + 0.1 M HClO₄ solution, (a) $t_{\text{growth}} = 15$ min; (b) $t_{\text{growth}} = 45$ min; (c) at $E_N = 0.200$ V, $t_N = 0.04$ s, $E_L = 0.600$ V, $E_U = 1.020$ V, $f = 100$ Hz, $t_{\text{growth}} = 45$ min, and in 0.2 mM PdCl₂ + 0.1 M HClO₄ solution. (d) The ratio of edge atoms to total surface atom on THH{310} with increasing size of THH NCs.